

REMARKS

Claims 1, 10 and 18 have been amended to include the limitations of allowable Claim 22. Notably, it has been claimed that the postcrosslinking is effected by a crosslinker which is a compound containing two or more groups that form covalent bonds with the carboxyl groups of the polymer.

One of ordinary skill in the art understands the term “postcrosslinked” in Claim 1 as “crosslinked after polymerization”. The postcrosslinking is not a polymerization. The postcrosslinking is a crosslinking between existing polymer chains. This is confirmed by of “Modern Superabsorbent Polymer Technology” on page 97, last paragraph to page 98, first paragraph (attached herewith):

“Any compound that can react with two or more functional groups on the polymer backbone can function as a surface crosslinking reagent. For superabsorbents, this requires reagents that can react with the carboxylic acid or carboxylate moieties on separate, adjacent polymer chains.”

“Modern Superabsorbent Polymer Technology” mentioned useful postcrosslinkers on page 98, first paragraph:

“These surface crosslinking agents include polyhydric alcohols,^{49,50} glycidyl compounds,¹⁰¹⁻¹⁰³ and alkylene carbonates.^{104,}”

The reaction mechanisms are described on pages 59 and 60 (Schemes 2.5 to 2.7).

Applicants have now claimed that the postcrosslinking is effected by a crosslinker which is a compound containing two or more groups that form covalent bonds with the carboxyl groups of the polymer.

Therefore all rejections of record should be withdrawn.

This application presents allowable subject matter, and the Examiner is kindly requested to pass it to issue. Should the Examiner have any questions regarding the claims or otherwise wish to discuss this case, he is kindly invited to contact Applicants' below-signed representative, who would be happy to provide any assistance deemed necessary in speeding this application to allowance.

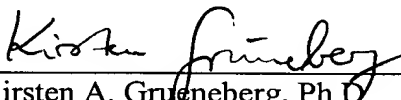
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Modern Superabsorbent Polymer Technology



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crosslinks in each molecule. However, because of the rapid depletion of the crosslinker, by 90% conversion the distance between crosslinks would be 1,000,000 g/mol. In conjunction with the much lower M_n being formed at this time, the number of crosslinks per chain would be below one, on average. In other words, these chains would not be part of the network at all.

Superabsorbents with lower amounts of extractable polymer, and thus potentially better properties, could presumably be prepared by using a crosslinker that is more uniformly incorporated. The higher r_1 value for the polymerization of unneutralized acrylic acid and TMPTA implies a slower rate of incorporation for the crosslinker, thus leaving more available for reaction later in the polymerization. In a similar ^{13}C -NMR study of allyl end-capped polyethylene oxide crosslinkers by Smith et al.,¹⁰⁰ more uniform incorporation of the crosslinker than in the case of TMPTA was found.

At variance with the simulation above is the fact that rather low levels of extractable polymer can be achieved when preparing crosslinked poly(acrylic acid) superabsorbents, even though the crosslinker is depleted earlier in the polymerization. This may be due to grafting reactions onto the gel network by the polymer chains made later in the polymerization. Grafting onto a pre-formed polymer is well known in emulsion, suspension, and solution polymerizations.¹⁰¹ Tobita¹⁰² has addressed the issue of chain transfer to polymer in both emulsion and solution processes. Grafting is believed to occur at high conversion in solution processes, while in emulsion processes some grafting occurs even at low conversion. In a solution process, the high concentration of polymer and low concentration of monomer at the end of the polymerization favor grafting. The model of an inhomogeneous crosslinked network in the polymerization of crosslinked poly(acrylic acid) superabsorbents, resulting from the high reactivity of the crosslinker, is consistent with Tobita and Hamielec's modeling¹⁰³ of the crosslinked system of methyl methacrylate and EGDM. Organic azo compounds, such as azobis(isobutyronitrile) and 2,2'-azobis(2-amidinopropane) hydrochloride, are known to be rather poor hydrogen abstractors, which results in much lower efficiency of grafting.¹⁰⁴ Persulfates, on the other hand, are quite active in hydrogen abstraction.¹⁰⁵

Extractable polymer can be formed by a variety of mechanisms besides the lack of incorporation of crosslinker. Chain transfer that prematurely terminates growing chains, chain degradation, and cleavage of crosslinks already formed are particular examples. Commercial superabsorbents typically contain 5%–20% extractable polymer, and significant attention is paid to maintaining a low level for performance reasons.¹⁰⁶ If the extraction is extended over a long time, the low-molecular-weight linear chains diffuse from the crosslinked particles first, and the high-molecular-weight chains follow, as illustrated by the data in Figure 2.15.

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2.7.1. Surface Versus Bulk Crosslinking

The other mode of network formation is curing or post-polymerization crosslinking, similar in principle to the processes used in the manufacture of rubbers. An agent, at

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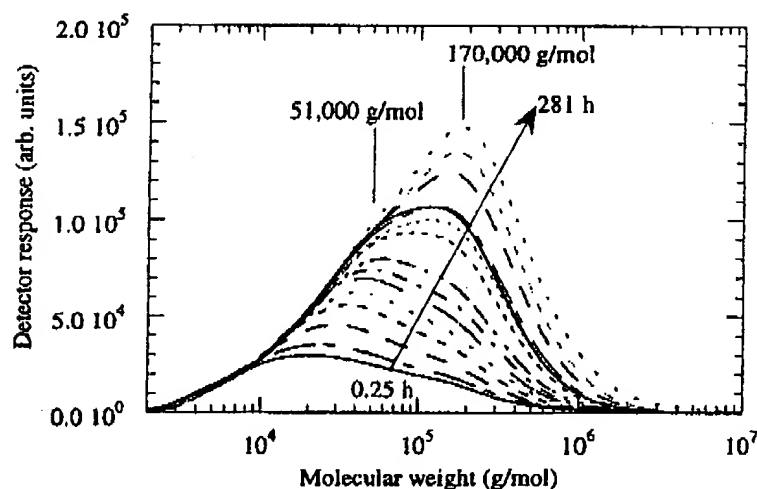


Figure 2.15. The molecular weight distribution of extracted soluble polymer as a function of extraction time. As extraction time increases from 0.25 to 281 h, the peak in the molecular weight distribution increases from about 10^4 g/mol to about 1.7×10^5 g/mol for a sample made by the process of Burgert et al.¹¹⁸ (D. S. Allan, The Dow Chemical Co., unpublished results.)

least di-functional (or potentially so), is first mixed with pre-formed polymer chains, and a coupling reaction between the agent and functional groups on the polymer chains is then triggered. Decoupling the mixing from the curing reaction is frequently accomplished by low temperature mixing followed by heating.

Two different types of post-polymerization crosslinking agents have been used in the manufacture of superabsorbents, ionic and covalent, and these are discussed separately below. An important implication of post-polymerization crosslinking, in the case of absorbents, is the capability of increasing the crosslink density near the surfaces of gel particles. The advantages of doing this are discussed at length in Chapter 5. It is not uncommon for commercial products to be crosslinked in the bulk via co-polymerization and subsequently treated with either ionic or covalent agents to increase the crosslink density on the particle surface. Specific processes are described in Chapter 3, section 3.2.8.1.

2.7.2. Ionic Crosslinking

Multivalent cations can associate with more than one carboxyl group on polycarboxylated chains, forming at least a transient crosslink. For example, it is well known that a severe reduction in swelling capacity of polyacrylates occurs in the presence of calcium ion, as shown in Figure 2.16. Presumably the divalent cation in the external swelling liquid diffuses throughout the gel, and causes its catastrophic collapse by over-crosslinking. To diffuse, the cation dissociates from at least one

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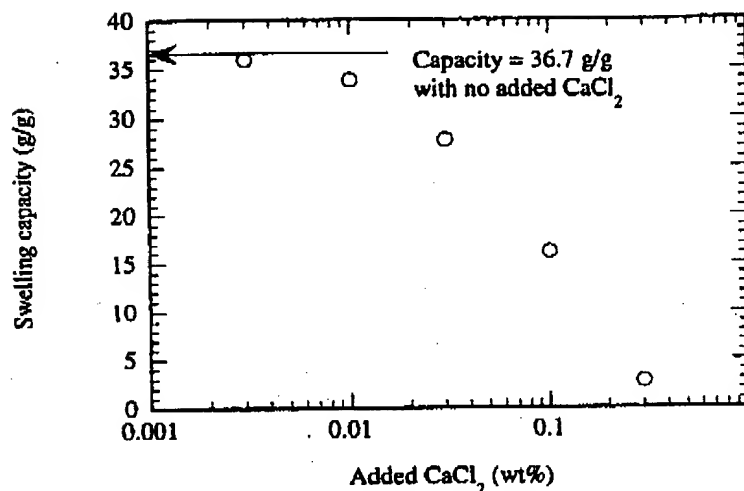


Figure 2.16. Impact of added calcium ions on swelling of crosslinked sodium polyacrylate in 0.9% NaCl.

site at a time and moves through the bulk of the gel, probably in a series of jumps. With trivalent ions, diffusion through a gel may be slower since at least two association sites must release to allow enough chain relaxation for the ion to move to a new location. Indeed, trivalent (or higher) ions such as aluminum can serve as useful crosslinkers. A review of much of this chemistry can be found in the thesis from Princeton University by Uhl.¹⁰⁷

To use metallic ions as general purpose, post-polymerization crosslinkers requires contacting all portions of the gel mass uniformly. This is naturally difficult since the diffusion of Al^{3+} ions through the polyelectrolyte network is slow. High dilutions of polyelectrolyte and aluminum ion could be used, but this would require subsequent removal of large amounts of water since the final superabsorbent product must be substantially dry. Complexing agents such as citric acid have been used to delay association with the network relative to diffusion. Ionic crosslinking has been used for *pre*-polymerization crosslinking as well.¹⁰⁸ This procedure appears equivalent to preparing aluminum triacrylate *in situ* and incorporating it as a copolymerized crosslinker.

Surface treatment of polycarboxylated polymers with aluminum ions was first patented by Ganslaw and Katz in 1977.¹⁰⁹ The stated purpose was to improve dispersibility. An alcohol-water mixture was preferentially used to distribute the aluminum compound. Surface treatment of particulate gels with aqueous solutions of aluminum compounds has been shown to improve absorption under pressure.

Ionic post-treatments are essentially room temperature processes. As noted, separating the diffusion from the binding is difficult, and hence the crosslinking occurs primarily on the surface of the gel. An indication of the diffusion of aluminum can

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be inferred from the micrographs obtained by electron microprobe analysis (EPA) shown in Figure 2.17. This technique utilizes an electron microscope to map the concentration of individual elements across the sample. For these images, superabsorbent particles were swollen in aqueous aluminum sulfate solutions at a ratio of 10 g of solution to 1 g of polymer. The resultant gels were allowed to stand at room temperature for different time periods and then dried in a forced air oven at 165°C. Particles were mounted in epoxy, sliced, polished, and mapped for sodium and aluminum using EPA. The gel of Figure 2.17a was allowed to sit for 15 min before drying, while the gel of Figure 2.17b sat 16 h. The diffuse distribution of the aluminum ion in the latter sample is apparent.

Polyquaternary ammonium salts may also be used as crosslinkers. To be an effective crosslinker a species must contain at least two charged sites. The patent art suggests that multisited polyquaternary compounds perform best.^{110,111} The preferred molecular weight used by Alexander et al.¹¹⁰ is 300–4,000 g/mol; an example reagent is MAGNIFLOC 579C polyamine obtained from American Cyanamid Company. In this work the original polyacrylate substrate was already crosslinked, and the polyquat was added as a surface treatment to increase "both the rate of water absorption and the quantity of water absorbed and retained by the resin."

2.7.3. Organic Reactions With Carboxylic Acids

Esterification of the numerous pendent carboxyl groups on typical superabsorbents is another common strategy for post-polymerization crosslinking, illustrated generically in Scheme 2.5. An example is the use of polyhydroxy compounds as claimed in a patent to Tsubakimoto et al.¹¹² In the example, glycerol is added in an aqueous isopropanol mixture to the surface of dried and sized gel particles.

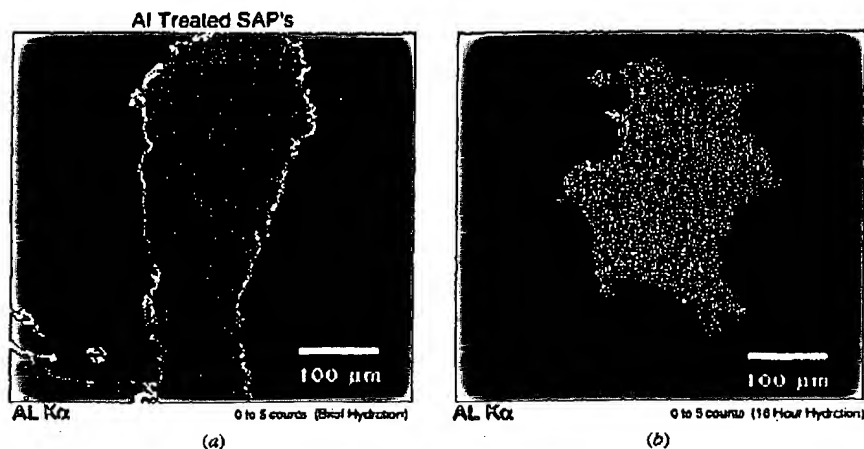
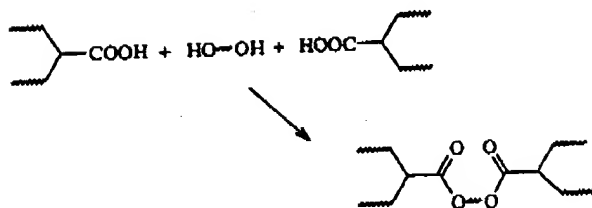


Figure 2.17. Micrograph showing diffusion of aluminum into a superabsorbent polymer swollen in water for 1 (a) 15 min or (b) 16 h. (C.K. Black, The Dow Chemical Co., unpublished results.)

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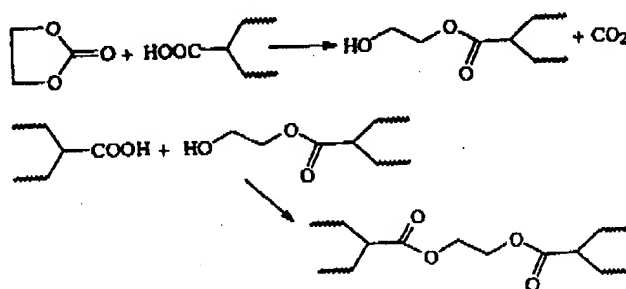


Scheme 2.5

This solvent mixture improves the uniformity of crosslinker distribution among the particles as well as modulating its penetration into each particle. The treated particles are then heated to around 200°C for several minutes. In addition to ester linkages, amide groups, formed from the reaction of polyamines with the carboxylic acid groups, may be used for crosslinking, but this reaction is more sluggish.¹¹³ A more detailed discussion of the processes of these and the remaining methods of post-polymerization crosslinking are given in Chapter 3, section 3.2.8.1.

Dahmen and Mertens¹¹⁴ have described the use of organic carbonates, especially ethylene carbonate in aqueous solution, for surface crosslinking; their approach avoids the use of flammable alcohols. A condensation reaction occurs producing carbon dioxide and a hydroxyethyl moiety that subsequently reacts with the available carboxyl groups to form ester bonds as crosslinks.¹¹⁵ Both reactions are illustrated in Scheme 2.6.

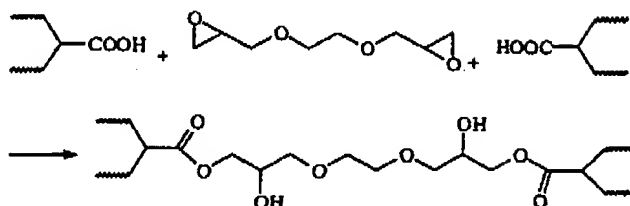
Several patents disclose the use of diglycidyl compounds, particularly ethylene glycol diglycidyl ether (EGDGE), to effect surface crosslinking,^{116,117} as shown in Scheme 2.7. A typical approach is to add a mixture of EGDGE and a solvent to the surface of dried and sized gel particles. These coated particles are then heated at approximately 150°C for generally at least 20 min. As with other systems, the depth of penetration, and thereby the crosslink density of the outer surface, can be controlled to some extent by the water concentration in the coating mixture.



Scheme 2.6

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Scheme 2.7

Crosslinks internal to the gel particle, rather than on the surface, can also be obtained through post-polymerization esterification. This naturally requires the thorough incorporation of the reagent into the reaction mixture. An example of this approach is a process wherein polyethylene glycol is added to the polymerization recipe.¹¹⁸ Separate from the crosslinking reaction, but also cited in the same application, is controlled degradation of the polymer network from oxidation by small amounts of sodium chlorate added to the polymerization mixture. This oxidizer is largely inert through the polymerization and drying operations but is activated during the heat treatment step that effects the esterification. This controlled breakdown of the polymer network in the center of the particle is thought to lead to a core/shell structure in the particle, which the authors speculate is responsible for the demonstrated improvement in modulus relative to swelling.

2.8. COMPUTER MODELING OF GEL POLYMERIZATION

The behavior of a complex system, such as the formation of crosslinked sodium polyacrylate gels discussed in this chapter, cannot be easily predicted with a single rate equation. Particular problems in this case are the extremely rapid propagation rate of acrylic acid, the early incorporation of crosslinker, and the inability of crosslinked gels to flow, all of which combine to make heat removal especially difficult. This situation would suggest that to maintain temperature control it would be advantageous to operate at low concentrations, but it is costly to remove large amounts of water. Interacting factors such as these are inducements to utilize elaborate computer models to predict behavior.

While development of a computer model for gel polymerization could begin with choosing among the many platforms available, there are elements that are common regardless of this choice. The discussion here will be sufficiently general to be applicable to many different hardware and software systems.

A model of gel polymerization could incorporate any of the reactions outlined in this chapter. However, central to any model is the numerical integration of the propagation equation from the initiation of polymerization to the time of interest, first shown in Eq. 2.5 and reproduced more generally in Eq. 2.38:

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